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End Semester Examination of Semester–I, 2015
Subject : CHEMISTRY (PG)
Paper : CEM–102 (Theory) (Inorg.)
Full Marks : 40
Time : 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

Illustrate the answers whenever necessary

Attempt one question from each group

Group A

1. a) Write the matrices corresponding to operations generated by proper rotation at an angle θ. 3

   b) How many symmetry operations will be accounted in D_n and D_{nd} point groups? 2

   c) Name the symmetry elements and hence the point group (any two). 3

   $PtCl_4^{2-}$, $Co(en)_3^{2+}$, MnO_4^-, PCl_5

   d) Show that S_3 and C_{3h} represent the same group. 2

2. a) Construct the character Table of C_{3V} point group explaining the principles involved and assign Mulliken symbols to the Irreducible representations. 3

b) For C_{2V} the reflection operations belong to different classes while in C_{3V} all the reflections operations belong to the same class — explain. 3

c) Constitute reducible representation for motional degrees of freedom in H_2O. Calculate the irreducible representations in it.

The character Table for C_{2V} Point Group is given below :

C_{2V}	E	$C_2(z)$	$\sigma_V(xz)$	$\sigma_V(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

Group B

3. a) Write the Styx number of the following compounds from the rules that govern them : 3

i) B_4H_9

ii) B_5H_{11}

b) Use Wade's rule to predict the structures of the following compounds : 2+2

i) $Rh_6(CO)_{16}$

ii) $Co_3(CO)_9CCl$

c) What is Octahedral Site Preference Energy (OSPE)? Using example explain its significance. 3

4. a) What is synergic effect? Explain with an example.2

b) $Cr(H_2O)_6^{2+}$ is labile but $[Cr(CN)_6]^{4-}$ is inert. Explain. 2

c) Give the structure and bio-function of rubredoxin. 3

d) Explain the 'trigger mechanism' suggested by Perutz for O_2-binding of deoxy-Hb. 3

Group C

5. a) What are 'static' and 'dynamic' Jahn-Teller distortions. Give example of each. 3

b) d^3 and d^8 metal ions show preferences for octahedral geometry over tetrahedral geometry — explain. 3

c) Explain the M–M multiple bonding with respect to edge sharing bioctahedra and tetragonal prism. 4

6. a) Explain the differences in structural features between deoxy-Hb and Oxy-Hb. 4

b) How is Ca^{2+}-estimated by Na_2EDTA titration? Specify pH and indicator? 3

c) Pt(II) forms Zeiss's salt but Ni(II) and Pb(II) do not form analogous salts — explain. 3

Group D

7. a) What is homotropic allosteric effect in O_2-binding of deoxy-Hb? 3

b) Give the structure and bio-function of 4Fe-4S protein. 3

c) Rationlize the observed logK values at 30^0C

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4(en)]^{2+} + 2H_2O; \quad logk_1 = 10.7$$

$$[Cu(H_2O)_4(en)]^{2+} + en \rightleftharpoons [Cu(H_2O)_2(en)_2]^{2+} + 2H_2O; \quad logk_2 = 9.3$$

$$[Cu(H_2O)_2(en)_2]^{2+} + en \rightleftharpoons [Cu(en)_3]^{2+} + 2H_2O; \quad logk_3 = -0.9$$

d) Write a note on (any one) : 2

Fe(IV), Ni(III)

8. a) State the bio-function of himerythrine. 2

b) Discuss the application of fullerene in medicine. 2

c) What is spin-state equilibrium? Explain the effect of temperature and pressure on it? 1+2

d) Octahedral Ni(II) complexes give sharp and symmetrical electronic spectra while such spectra of Cu(II) complexes are broad and unsymmetrical. Justify. 3